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THE USE OF MEDICAL CHELATING AGENTS FOR THE REMOVAL OF IRON STAINS FROM MARBLE

ANNA FUNKE, LEAH POOLE, JASON CHURCH, DR. MARY STRIEGEL, AND MARTHA SINGER

Chelating agents have long been used by conservators to remove iron stains from historic stone. The chemical composition of marble, however, presents a particular challenge because its main component—calcium carbonate—is highly sensitive to acidity and chelating agents are acidic by nature. Chelators chemically bond with metal ions, making them removable with water. This allows conservators to simply wash away metallic stains. While chelating agents are generally extremely effective at removing iron stains, their acidity can be damaging to the marble substrate. While these effects can be minor and limited to dulling a marble surface, they can be much more severe and even result in the permanent etching of the stone. This study looks specifically at the use of chelating agents, which are chemically analogous to chelators used in the medical profession to treat heavy metal poisoning and similar conditions. These products are therefore highly stable and well understood, as they have been through rigorous analysis and testing to gain approval for medical use.

This study investigates the use of five different chelating agents for their efficacy in the removal of iron stains as well as their physical and chemical effects on marble surfaces: ammonium citrate, cysteine, maltol, picolinic acid, and thioglycolic acid. One group of samples cut from Colorado Yule marble is artificially stained with iron oxide while another group is left unstained. Each chelating agent is tested at two different pH values that were chosen through UV-visible spectroscopy. The samples are analyzed before and after cleaning. Colorimentry, glossimetry, and laser profilometry readings are taken of all samples at each state of this study in order to establish a thorough understanding of how these chelating agents affect the physical properties of the marble surface and to quantify the effectiveness of the chelators in removing the iron stains. Surface readings of the pH values of the samples as well as FTIR spectra are also taken at each stage in order to gain a better understanding of the chemical effects that the chelating agents have on the marble surface.

KEYWORDS: Iron stains, Marble, Chelating agents, Chelators

1. INTRODUCTION AND REVIEW OF PREVIOUS RESEARCH

Conservators have long used chelating agents to remove metal stains from stone. However, when applied to marble, this poses complex chemical challenges. Calcium carbonate, which makes up a large proportion of marble, has a pH of approximately 10.3. Chelating agents, however, are acidic by nature. This means that, unless highly buffered, they can cause significant damage to marble by etching or even dissolving the calcium carbonate of which it is composed. Therefore, the goal of this study was to identify a chelating solution that effectively reduces iron stains without causing significant damage to the marble substrate.

This research was started by Martha Singer several years ago, who investigated the use of medical chelating agents for the removal of iron and copper stains from marble. Medical chelating agents are used for the treatment of heavy metal poisoning and similar afflictions. They are chemically engineered to target specific harmful metal ions while leaving behind all others (Crisponi and Remelli 2008, 1227). This potential for a more targeted approach held great promise for nuanced treatments in the conservation of historic objects and structures.

Singer identified two medical chelating agents to test: the copper chelator d-penicillamine (Merck) and the iron chelator Desferal (Novartis Pharmaceuticals). However, these products are too expensive for most conservators. Singer therefore identified two alternative chelating agents with analogous functional groups to use instead of the more expensive medical products. The copper chelator cysteine was used instead of d-penicillamine, and the iron chelator acetohydroxamic acid was tested instead of Desferal. Interestingly, despite their specific design, Singer found that cysteine performed significantly better at the removal of iron stains than acetohydroxamic acid.

Singer's research was continued by Leah Poole in 2014. Poole focused on establishing the pH value at which different iron chelating agents could be effectively used on marble while causing minimal effect on the calcium carbonate. She did so through test tube–based analysis using UV-visible spectroscopy. Poole tested the chelators from Singer's original study, cysteine and acetohydroxamic acid, as well as ammonium citrate, maltol, and picolinic acid, which are more commonly used in conservation. She tested each chelating agent at the pH values 7.4, 8.5, 9.2, and 10. Her tests determined that ammonium citrate, cysteine, maltol, and picolinic acid performed best at pH 9.2 and pH 10. Acetohydroxamic acid, however, was most effective at pH 8.5 and pH 9.2. Acetohydroxamic acid was once again among the least successful treatment solutions.

2. MATERIALS

As acetohydroxamic acid did not show promising results in either the Singer or Poole study, further testing on this chelating agent was not pursued. Instead, thioglycolic acid was added to the study because this agent had shown promising results in conservation (Thorn 2005, 891). The agents tested were, therefore, ammonium citrate, cysteine, maltol, picolinic acid, and thioglycolic acid.

3. EXPERIMENTAL METHOD

3.1 Preparation of Treatment Solutions

Each chelating agent was prepared at a concentration of 0.15 M (mol). This concentration was established by Poole using visible spectroscopy. Different ratios of chelating agent were added to ferric nitrate to establish how the chelating agent complexes with iron (III). Maltol, however, was prepared at a concentration of 0.09 M owing to its very low solubility in water. A small amount of sodium hydroxide had to be added to the maltol solution from the beginning because it dissolves more readily in alkaline solutions. A solution of 1 M sodium hydroxide was used to buffer these solutions to the desired pH values: one solution of pH 9.2 and one solution of pH 10 was prepared for each chelating agent based on optimal pH values determined in the Poole study. Thioglycolic acid and picolinic acid both have buffer zones just above pH 7, which made their adjustments more difficult. Once the pH reached the buffer zone, it became extremely sensitive and would fluctuate significantly with the addition of every drop of sodium hydroxide. Therefore, a 5% solution of hydrochloric acid was used for back titration to bring the solutions to the desired pH value.

An electrode pH reader was used to continuously monitor the pH of the solutions as they were being prepared. It would have been very difficult to achieve the precise values with less precise equipment.

3.2 Samples

3.2.1 Sample Preparation

A total of 63 samples were prepared from Colorado Yule marble, which is a white stone with crystalline inclusions but without veins. This makes it easier to observe physical changes and provides greater consistency across the samples. The marble samples were approximately 4 cm in diameter and just under 1 cm thick (fig. 1). The back of each sample was engraved with a unique identification number. A notch was also engraved into the bottom rim of each sample to help me consistently position the samples in the same way throughout the data collection process. The surface of the samples was then polished to a

Fig. 1. Image of marble sample before staining or stain removal

smooth finish and placed in an ultrasonic cleaner to remove any loose marble dust. After this, they were left in the oven overnight at 70°C to remove any excess water and facilitate staining.

3.2.2 Staining

As has already been mentioned, both unstained and iron-stained samples were used in this study so that the chelating agents' effects on the iron stain as well as on the marble surface could be evaluated. Thirty samples were left unstained, three samples for each of the 10 treatment solutions. Thirty-three samples were artificially stained with iron oxide. This included three controls and three samples for each treatment solution to control for inconsistencies within the data.

Replicating natural iron staining was somewhat challenging. Ultimately, an effective system was devised using steel wool and timed sprinkling with water. I used steel wool because it is a readily available source of low-quality metal that both corrodes quickly and allows the free passage of water, carrying the staining corrosion product onto the marble. It turned out that the coarser steel wool corroded too rapidly; therefore, it was impractical. It quickly went beyond red iron (III) oxide (Fe_2O_3) and turned into black iron (II, III) oxide (Fe_3O_4). This caused a dark-gray deposit on the marble, which caused only very limited staining. Grade 0 (fine) proved to be the best for this study, as it corroded much slower and, therefore, only had to be exchanged once or twice a day. It also resulted in more staining with red iron (III) oxide.

The Grade 0 steel wool was fluffed up and placed evenly over the samples, which were placed on an elevated wire mesh so that they would not sit in a pool of water (figs. 2, 3). Allowing the water to drain was important because otherwise the samples would stay saturated and the marble wouldn't absorb the stain as readily. Fluffing out the steel wool turned out to be an important step as it allowed for more oxygen to enter the system, which produced more iron (III) oxide as opposed to iron (II) oxide.

The water was delivered into the system through automatic sprinklers that were operated on a timer. After several different settings were tested, the sprinklers were finally set to "on" for two seconds and "off"

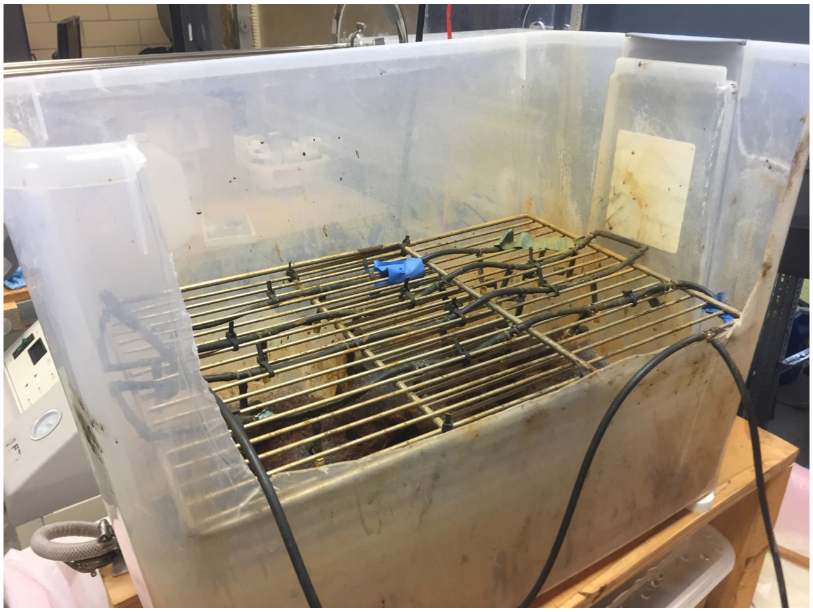

Fig. 2. The setup for staining the marble samples

Fig. 3. The marble samples during the staining process

for 30 seconds. It was important to let the samples dry slightly throughout the process and for the water to work on the steel wool before being washed away. The staining process took a total of 10 days. This included several days of testing and adjusting the sprinkler settings and changing back and forth between different grades of steel wool. Nevertheless, this process should be expected to take at least a week.

Once the staining was completed, the samples were placed in an oven overnight at 60°C. They were taken out the next morning and all loose iron oxide powder that had formed was brushed off, leaving behind only the engrained iron stain (fig. 4).

3.3 Methodology

3.3.1 Photography

Each sample was photographed before and after staining, as well as after each treatment. Photographs were taken from a consistent distance with a Nikon D5000 DSLR and a 35-mm lens. A gray scale and color scale was included in each image. These photographs provided an important record and reference throughout the study. They also helped to put into context the changes detected through other scientific methods and, thereby, determine what changes in data should be viewed as significant or noticeable to the naked eye.

3.3.2 Colorimetry

Colorimetry data were collected to quantify the visual changes that were affected on both the stained and unstained marble samples due to treatments with the different chelating solutions. The data were collected using a Chroma meter CR400, using the CIE L*a*b* color space. This model determines color by defining a point in three-dimensional space. It places the color along three axes: light to dark, red to green, and yellow to blue. Three readings were taken per sample. These readings were arranged in a vertical line down the center of each sample, as shown in figure 5.

Fig. 4. Marble samples after staining

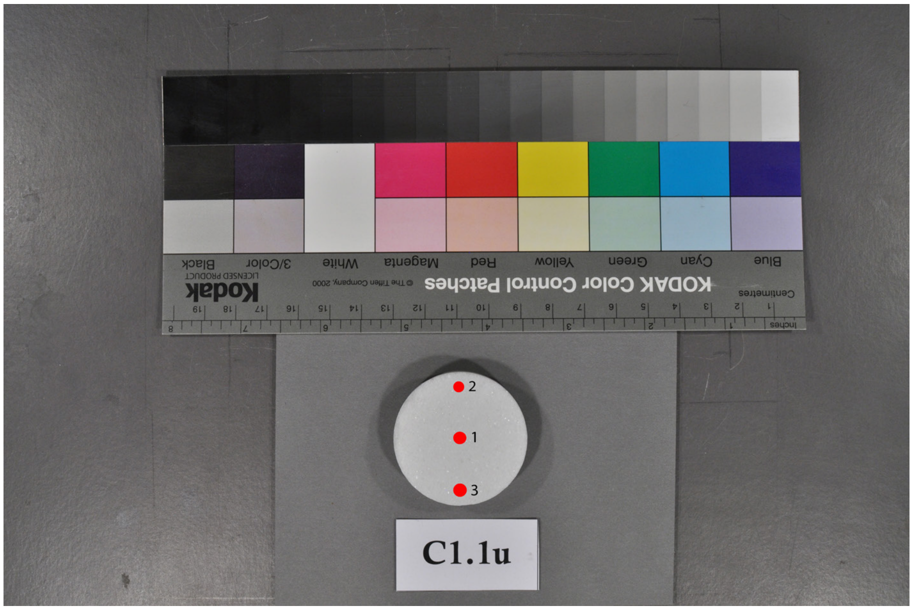

Fig. 5. Marble sample with red dots indicating the points where colorimetry data were collected

3.3.3 Glossimetry

Glossimetry was an additional method of analysis that was used to determine the physical changes undergone by the marble surface during treatment. The instrument used was a Gardener BYK micro-tri-gloss. This instrument can collect readings at three different angles of impact: 20°, 60°, and 85°. After some testing, it turned out that the readings taken at 85° were the most nuanced for the Colorado Yule marble, which is consistent with its low-gloss surface. The instrument automatically takes the average of three readings for each point that it measures. One reading was taken approximately in the center of each sample.

3.3.4 Laser Profilometry

Unlike the methods described so far, laser profilometry data were collected on only the first sample from each set of duplicates because of the length of time that it took to take the readings—approximately two hours per sample. This form of analysis collects an exact laser scan of a surface. These data were collected to determine whether the chelating agents were causing significant amounts of etching during treatment. Each reading was taken of an area 0.9 in. × 1.2 in. in the center of the sample. Within this space, 920 lines were scanned. Both the horizontal and vertical spacing was 25 mm, which results in a very high resolution.

3.3.5 Surface pH

The surface pH of each sample was taken before and after treatment. The natural pH of Colorado Yule marble is generally between 9.4 and 9.6. Therefore, any substantial decrease or increase would indicate significant chemical changes in the marble surface. The instrument used was a Thermo Scientific Orion Star A326 pH/RDO/DO meter with an Orion 8135BNUWP Electrode. Before each test, the electrode was calibrated using pH 4.01, pH 7, and pH 10.01 buffers. Five drops of deionized water were placed in the center of the sample; then, the reading was taken. It could take a surprisingly long time for the reading to stabilize. Especially after treatment, it could take up to several minutes. The electrode was rinsed with deionized water after each reading and kept in storage solution while each sample was prepared. After approximately 30 samples, the readings would sometimes start to become inconsistent. In this case, the electrode would be recalibrated before further readings were taken.

3.3.6 FTIR

FTIR data were collected to determine whether the chemical composition of the marble was altered in any way by the treatments. The instrument used was a PerkinElmer Spectrum One FTIR Spectrometer. The background reading was taken using a 2.5-cm golden mirror. Three samples were selected to provide the readings for the marble before treatment. Only three were randomly selected because all samples were cut from the same stone and, therefore, should be chemically identical. This hypothesis was consistent with the results of the readings, which yielded three nearly identical spectra (fig. 6). The samples selected were C1.2s, L1.2u, and M1.2u. As with laser profilometry, only one sample from each set of duplicates was used to collect FTIR data because of the high levels of consistency with this form of analysis. However, when unusual results occurred, further duplicates were tested to ensure the accuracy of those results. The second sample from each set of duplicates was used for the collection of FTIR data. Transmittance spectra were collected for this study as a matter of instrumental convenience.

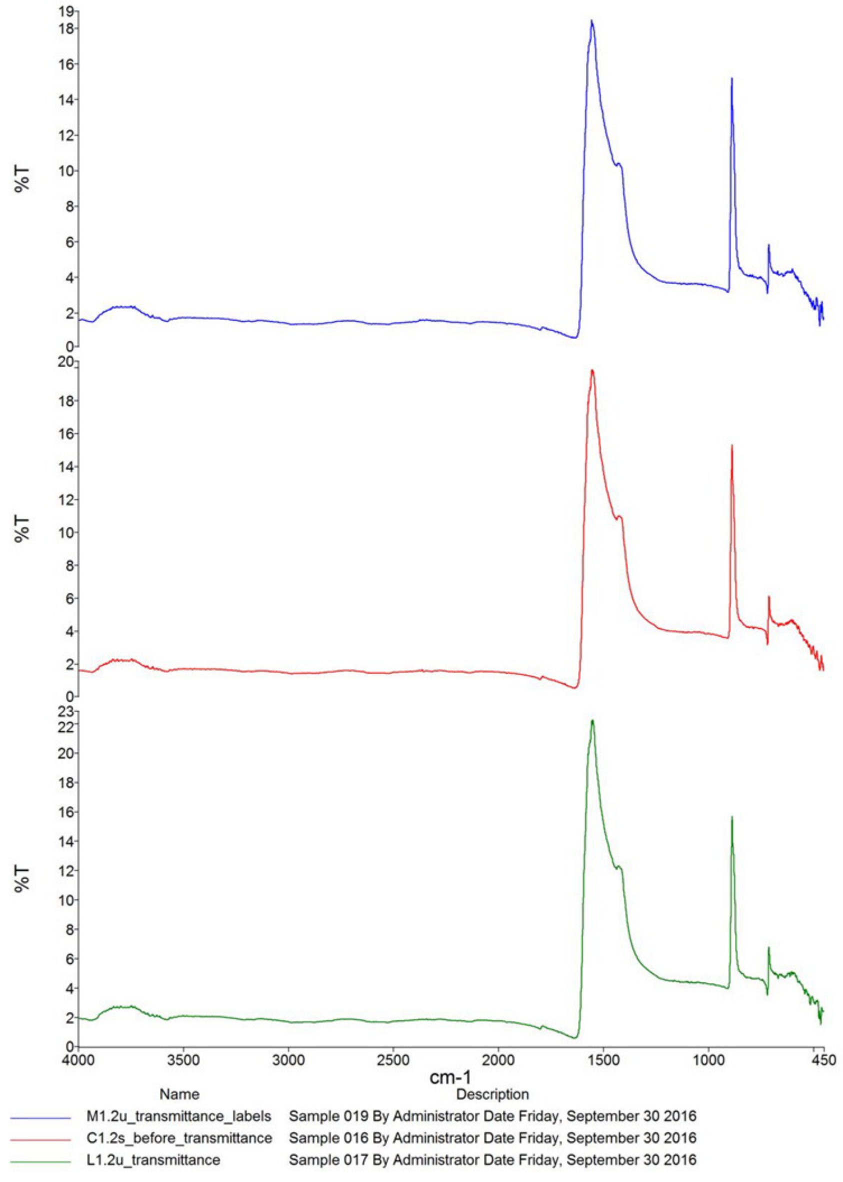

Fig. 6. FTIR spectra of the three marble samples without staining or treatment

Fig. 7. Setup of the treatment

3.4 Treatment Setup

The samples were suspended so that the lower half of the sample was submerged in the treatment solution. They were held in suspension for 30 minutes. This long dwell time was chosen to replicate a worst-case scenario in which a poultice might be left on for too long or a treatment solution is accidentally spilled on the object. Shorter dwell times and different application methods were not studied, although these would be interesting avenues for future investigation. The setup of the treatment can be seen in figure 7.

Once the samples were removed from their treatment bath, they were thoroughly rinsed with deionized water. Any excess treatment solution was dabbed off the samples with tissue paper. The samples were then air dried. Every sample was treated once, and one sample from each set of duplicates was treated a second time several days later to determine whether any of the treatment solutions would affect the samples differently after repeat treatments.

4. RESULTS

4.1 Colorimetry

The colorimetry data were crucial because they quantified the visual changes that took place both on the unstained and stained marble. For the unstained samples that underwent treatment, the final data readings were compared with those of pure marble that had not been treated in any way. The final data readings of the stained samples were compared with those taken of the freshly stained samples that had not been treated with a chelator. The difference between these values is expressed by the ΔE value. The formula to establish this value is as follows:

$$\Delta E = \sqrt{(\Delta L^2 + \Delta a^2 + \Delta b^2)}.$$

Most of the unstained samples were not changed significantly by the different treatments. The exceptions were those chelated by the cysteine and maltol solutions. Both the pH 9.2 and pH 10 solutions of these two chelators caused obvious yellow staining on the white marble. While this yellow staining could not be detected in the iron-stained samples, it should be kept in mind when treating artifacts that have only very light staining. It could also affect the marble surrounding an iron stain and affect its aesthetic integrity.

For the stained samples, the best results were achieved by ammonium citrate pH 9.2, thioglycolic acid pH 9.2, cysteine pH 9.2, and picolinic acid pH 10. The success of cysteine pH 9.2, however, needs to be weighed against the yellowing that it caused in the unstained samples. This may not be of great significance in heavily stained objects but, once again, it should be kept in mind when working on only mildly stained objects.

4.2 Glossimetry

The results of the glossimetry readings varied widely. There were several instances in which the gloss levels of some samples within a duplicate set increased while those of another sample in the same set decreased. Furthermore, while there is no standard value of variation at which the human eye can detect changes in gloss level, the manufacturer of the instrument used states that a change in approximately three gloss units can be detected by the human eye. Only a very small minority of samples showed a change greater than three gloss units. Owing to the inconsistencies across the gloss data, I decided that it should not be included in the final interpretation of the data, as results may vary so widely during application in conservation practice. The changes that take place in the gloss levels were generally more significant in the stained samples than in the unstained ones. This may be a result of gloss being more easily detected in darker surfaces, or it could suggest that the changing gloss levels are more closely related to the iron staining and its removal than the specific chelating agent that is used.

4.3 Laser Profilometry

Laser profilometry was a particularly important form of analysis because etching of the marble substrate is the primary concern when using chelating agents to remove iron stains from marble. While this instrument quantifies the surface profile in several different ways, the key value on which this interpretation is based is the standard deviation of the height distribution. This value defines the difference between the lowest pits and the highest peaks. Laser profilometry showed that significantly more etching occurred on the unstained samples. This is defined by the numeric value assigned to the surface roughness—also referred to as the sq value—which increased with each treatment round. While the changes in surface roughness were not significant enough to be perceptible with the naked eye, it should be taken into consideration when working on only lightly stained objects. Maltol performed very well in this analysis. Cysteine pH 10 also did very well on the unstained samples, where it was second only to maltol 9.2. Picolinic acid pH 10 performed very well on the unstained samples. Thioglycolic acid performed well at both tested pH values. However, it caused substantially more etching after the second treatment. Therefore, a single application would be more prudent with this substance.

4.4 Surface pH

The staining process itself lowered the pH of each sample by approximately 0.5 for each sample. Maltol was the only chelating agent that did not lower the surface pH of the untreated samples at all. However, the other solutions lowered it only by relatively small margins. There was only one sample—which was treated with ammonium citrate pH 9.2—that had its surface pH lowered by slightly more than 1. Interestingly, fewer of the treatment solutions seem to lower the pH of the surface of the iron-stained samples than that of the unstained ones. This happens even when both sets of data are compared with the original surface pH of the marble, that is, before it was stained with iron (III) oxide. Therefore, the most significant change in surface pH seems to be caused by the iron stain itself. Nevertheless, maltol pH 10 performs the best both on the stained and unstained samples. Cysteine pH 10 performs very well on the stained samples but not on the unstained ones. Thioglycolic acid pH 10 and ammonium citrate 10, however, perform well on both. In this form of analysis, the chelating solutions prepared at pH 10 consistently perform better than those prepared at pH 9.2.

4.5 FTIR

The FTIR data were consistent across the board. The marble itself—calcium carbonate—was always the dominant component, showing up as a broad stretching band around 1600 to 1350 cm^{-1} with a sharp band around 900 to 700 cm^{-1}. This is typical of carbonates.

The edge in the shoulder of the broad band was raised and slightly smoothed out in the stained samples, as can be seen in figures 8 and 9. The smoothing out of the broad band caused by the iron staining made it somewhat harder to detect any additional changes caused by the chelating agents on the stained set of samples. These were easier to detect on the unstained set of samples.

The data collected from duplicate samples were remarkably consistent. The only difference tended to be the intensity of the bands, and these differences were very minor.

Picolinic acid and maltol, however, showed different levels of intensity compared with the other chelating agents. While the highest band for all other chelating agents averaged out at around 20%T, the highest band for maltol averaged at around 25%T and those of picolinic acid at around 15%T. The difference in the intensity of the bands did not seem to be linked to the pH values of the treatment solutions but rather to the chelating agent used.

The only chelating agent that seems to have a chemical effect on the marble surface is picolinic acid. Both at pH 9.2 and pH 10, treatment with this chelating agent adds a peak to the FTIR spectrum of the unstained samples. The broad band around 1500 cm^{-1} shows a small, sharp off-shoot at around 1600 cm^{-1}. Picolinic acid is the only chelating agent tested whose chemical structure could be broken up to form a N=C bond, which may be causing this peak. This small additional peak, however, is obscured in the iron-stained samples.

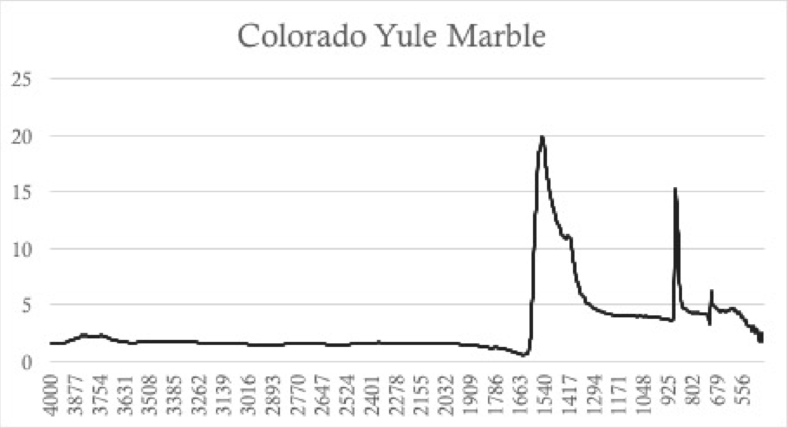

Fig. 8. FTIR spectrum taken on an unstained and untreated sample of Colorado Yule marble

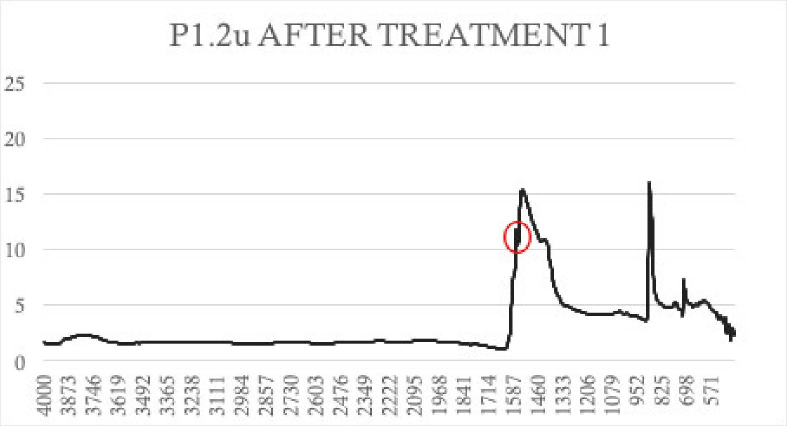

Fig. 9. FTIR spectrum of an unstained sample of Colorado Yule marble after it was treated with picolinic acid

It must be noted that, at this point, it is unclear what new compound forms on the marble surface as a result of the treatment with picolinic acid. While it is perfectly possible that this compound is safe and stable, we do not know at this writing. Therefore, I would recommend against the use of picolinic acid on historic objects until further research has been done. The use of picolinic acid could also interfere with future analysis if the chemical structure of the surface is altered through a treatment.

5. DISCUSSION

5.1 Maltol

While it can be said that maltol does not have any significant negative effects on a marble surface other than the yellow staining, it also does not seem to perform its key function of stain removal in a way that would justify its use.

5.2 Picolinic Acid

I would recommend against the use of picolinic acid in the removal of iron stains from marble until further research has been conducted on the results of the FTIR data owing to the compound that formed on the surface and its unknown effects on marble.

5.3 Ammonium Citrate

Ammonium citrate handles well as a product. It has a strong acidic smell when it is being prepared, but it is not very bothersome. It is easy to adjust its pH, as it does not have a buffer zone. It can cause eye and respiratory irritation but can safely be used outdoors and in well-ventilated spaces or with fume extraction.

While it did not cause any discoloration on the unstained samples in the form of yellowing, it did seem to darken the samples very slightly. Both the pH 9.2 and pH 10 solutions were among the top three performing solutions in terms of reducing the visual effects of iron staining.

The pH 10 solution caused negligible changes in surface pH and even increased it on the stained samples. However, the pH 9.2 solution caused some of the highest decreases in surface pH in the study. It should be kept in mind, however, that these changes were still below 1 point and, therefore, can be considered within the acceptable range of change.

The pH of the solution did not seem to matter with regard to the effect that the treatment had on the surface structure of the stained samples. Interestingly, the pH 10 solution seemed to cause more damage on the unstained samples than the pH 9.2 solution, which is rather counterintuitive. The changes caused to the surface of the stained samples were much more significant than those caused to the unstained ones. This is likely due to the removal of iron from the surface.

5.4 Cysteine

Cysteine does not pose any health or environmental hazards. It simply needs to be handled with care. Cysteine has quite a strong smell that lingers on the samples for a little while after treatment. However, it is not a particularly uncomfortable one. The pH can be adjusted very consistently, as it does not have a buffer zone.

Cysteine caused obvious yellow staining to the unstained samples. The staining seemed to remain water soluble, but this is nevertheless a very significant downside to this product if used on lightly or partially stained surfaces. It produced good results in terms of stain removal and the yellowing is not visible through heavy iron staining.

Cysteine pH 9.2 was the treatment that caused the most significant decreases in surface pH in this study on the unstained samples and the second most significant decreases in pH on the stained samples. Cysteine causes the second most significant change to the surface structure of both the stained and unstained samples after ammonium citrate. The exception to this was the use of cysteine pH 10 on the unstained samples, where it hardly caused any changes at all.

Cysteine is a surprisingly effective chelating agent for the removal of iron stains given that it is specially formulated to chelate copper ions. Nevertheless, it is a very successful product and could well be used both in the lab and in the field.

5.5 Thioglycolic Acid

Thioglycolic acid is the most hazardous substance in this study. It can cause severe damage to eyes and skin and is toxic when swallowed. It is also acutely toxic to aquatic life (category 3). This means that it can cause acute damage to aquatic life at concentrations of less than 100 mg/L. Thioglycolic acid is used at a much higher concentration when used as a chelating agent. However, it can easily be diluted. When used in a lab, it can be left to evaporate off in the fume hood. However, when used in the field, it must be managed carefully to limit the amount that enters the environment. A solid poultice should be taken back to the lab and allowed to dry out in the fume hood. Any liquid residue should be diluted as much as possible to prevent problematic amounts of contamination.

It should also be noted that thioglycolic acid has a very strong and unpleasant rotten smell, which requires fume extraction when working in the lab. This should also be considered before planning to do any big treatments in the field.

Like picolinic acid, thioglycolic acid has a buffer zone just above pH 7, which makes it difficult to adjust the pH of the solutions. Thus, it will require some back and forth adjustments using an acid (HCl) and a base (NaOH). A sensitive pH reader will be necessary to prepare these treatment solutions.

Finally, it should also be noted that while other chelating agents in this study can be purchased in solid form, thioglycolic acid is available only as a premade ~80% solution.

Thioglycolic acid hardly caused any color change on the unstained samples. Its pH 9.2 solution was very successful at reducing the iron stains. Its pH 10 solution did well after one application but did not seem to reduce any additional staining during the second application.

It caused only minimal changes to the surface pH of the samples. The pH 10 solution was particularly good in this regard, as it increased the pH of the stained samples and reduced the surface pH of the unstained samples by an average of only 0.05.

Thioglycolic acid also performed well in laser profilometry. It was consistently in the top five for both the stained and unstained samples. Again, it was much more successful in the first round of treatments, which suggests that if it were chosen for a treatment it should be applied only once and that repeat applications are probably not worthwhile.

6. CONCLUSION

As with most conservation treatments, no chelating agent provides the perfect solution for the removal of iron stains from marble. Using these agents at these high pH values reduces their efficiency substantially; however, this will often be a sacrifice worth making to preserve the original surface of the object by preventing serious damage through etching. It would be valuable to conduct further research on the best application methods for these chelating agents. This would be particularly interesting for cysteine, which caused heavy yellow staining of the white marble in this study but did not do so in the study run by Martha Singer. Applying the agent with a poultice may reduce or prevent staining. It would also be very interesting to further investigate the chemical changes caused by picolinic acid. This could help determine whether the resulting compound is stable or not. It could thereby help to establish whether this product should no longer be used in conservation and whether objects treated with it in the past may require retreatment.

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SOURCES OF MATERIALS

All chelating agents used in this study were purchased from Sigma-Aldrich.

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